



Polymers:
Random walk model

Polymers

- So far, we mostly talked about glasses as a group of noncrystalline materials
- Polymers are another important class of materials that are often found in noncrystalline form
- Polymers are long molecules composed of repeating units known as monomers.

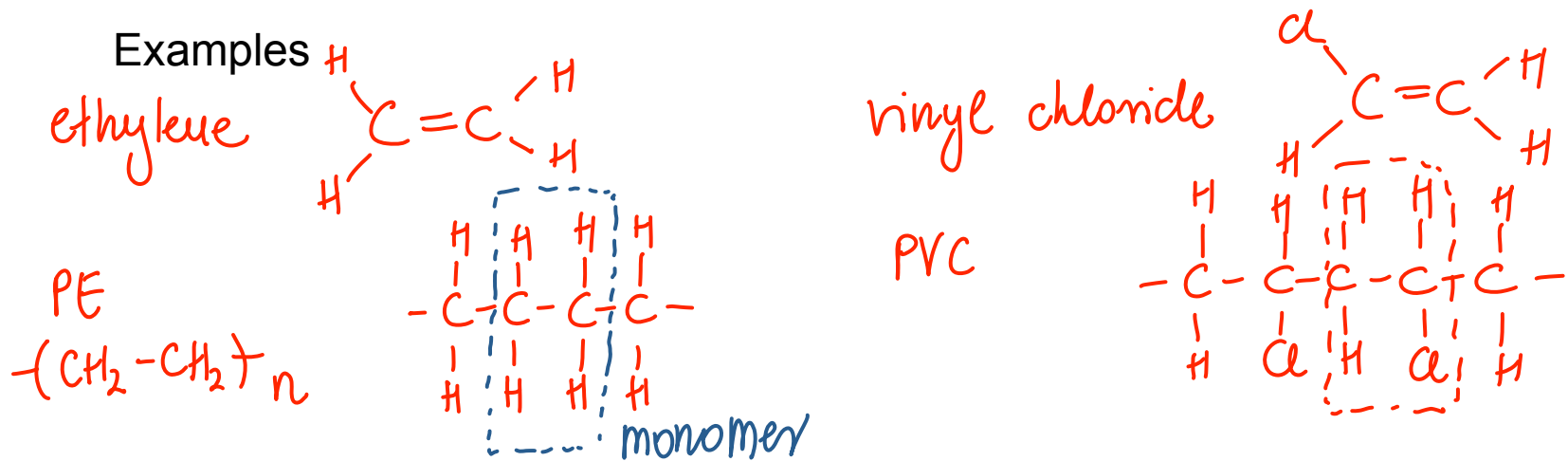
Poly mer
many parts / units

Ancient polymers

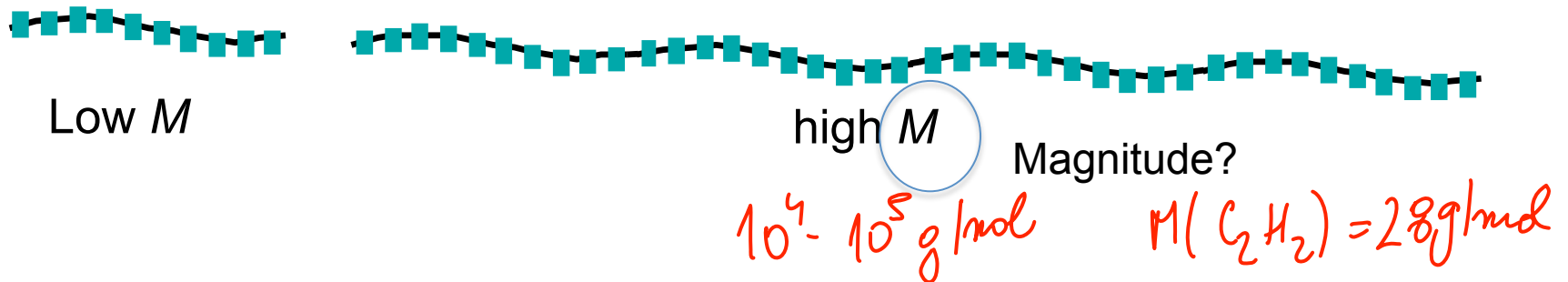
- Originally natural polymers were used
 - Wood
 - Cotton
 - Leather
 - Rubber
 - Wool
 - Silk
- Oldest known uses (real or fictional)
 - Rubber balls used by Incas
 - Noah used pitch (a natural polymer) for the ark
- Synthetic polymers: second half of 20th century
- Biopolymers: proteins, DNA, RNA

Polymers

- Most of polymers are *organic* in origin
- Many are covalently bonded *hydrocarbons* (composed of C and H), and sometimes *oxygen, nitrogen, sulfur, silicon, chlorine, and/or fluorine*



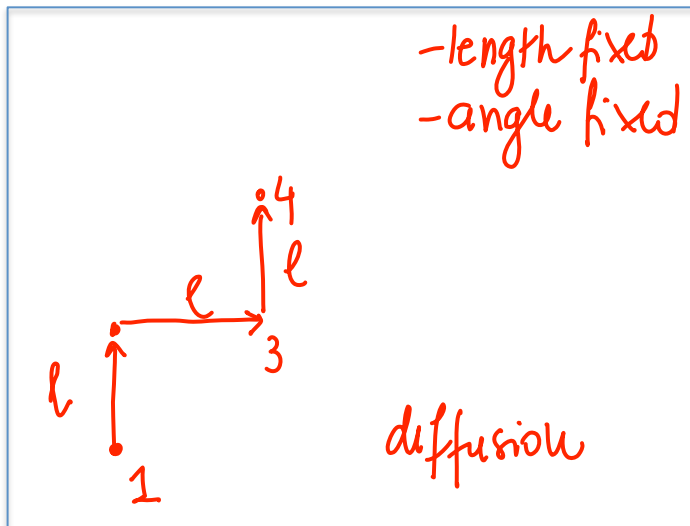
- Because of their large molecular weight (M), also referred to as macromolecules



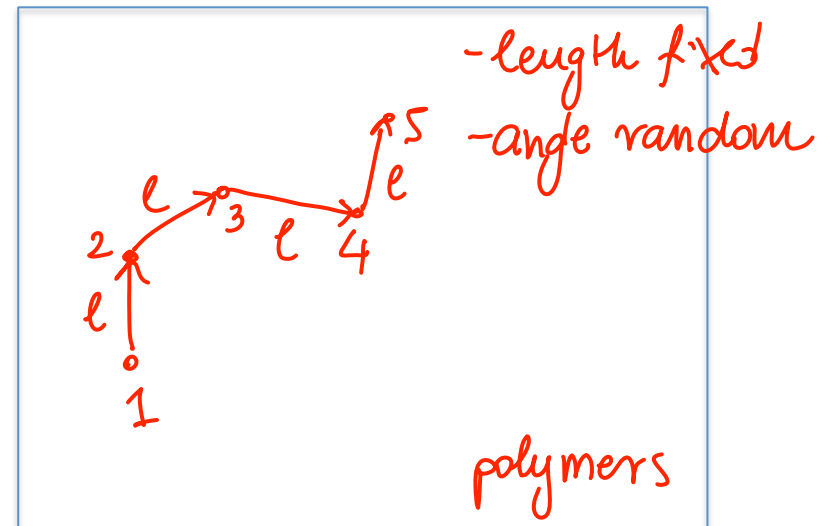
Random walk models

- How do we describe the structure of an amorphous polymer?
- We need a statistical average over the various conformations, able to provide us with as many information as possible → **random walk model**.
- A random walk denotes a path of successive steps in which *the direction of each step is uncorrelated with, or independent of, previous steps*—steps forward and backward, left and right, up and down are all equally probable.
- It is a rather general model applicable to other problems in MS&E: *gas diffusion or vacancy diffusion* (you might know it under the term of Brownian motion)

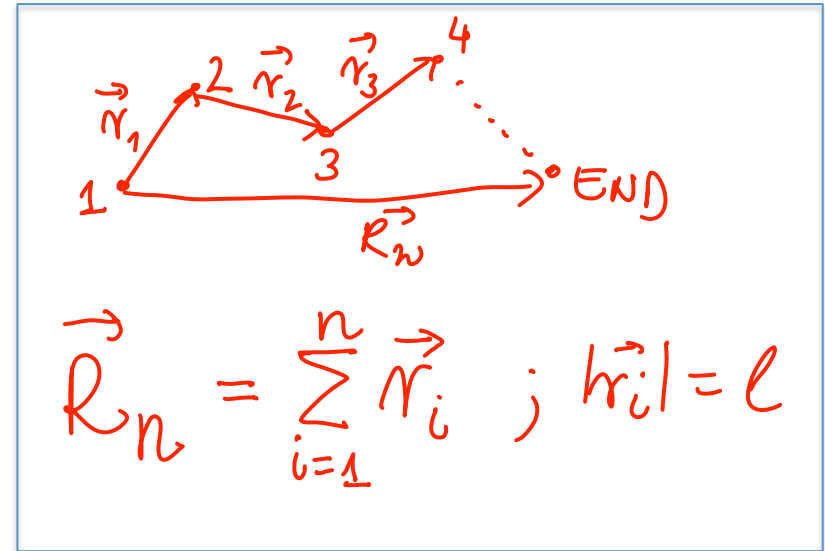
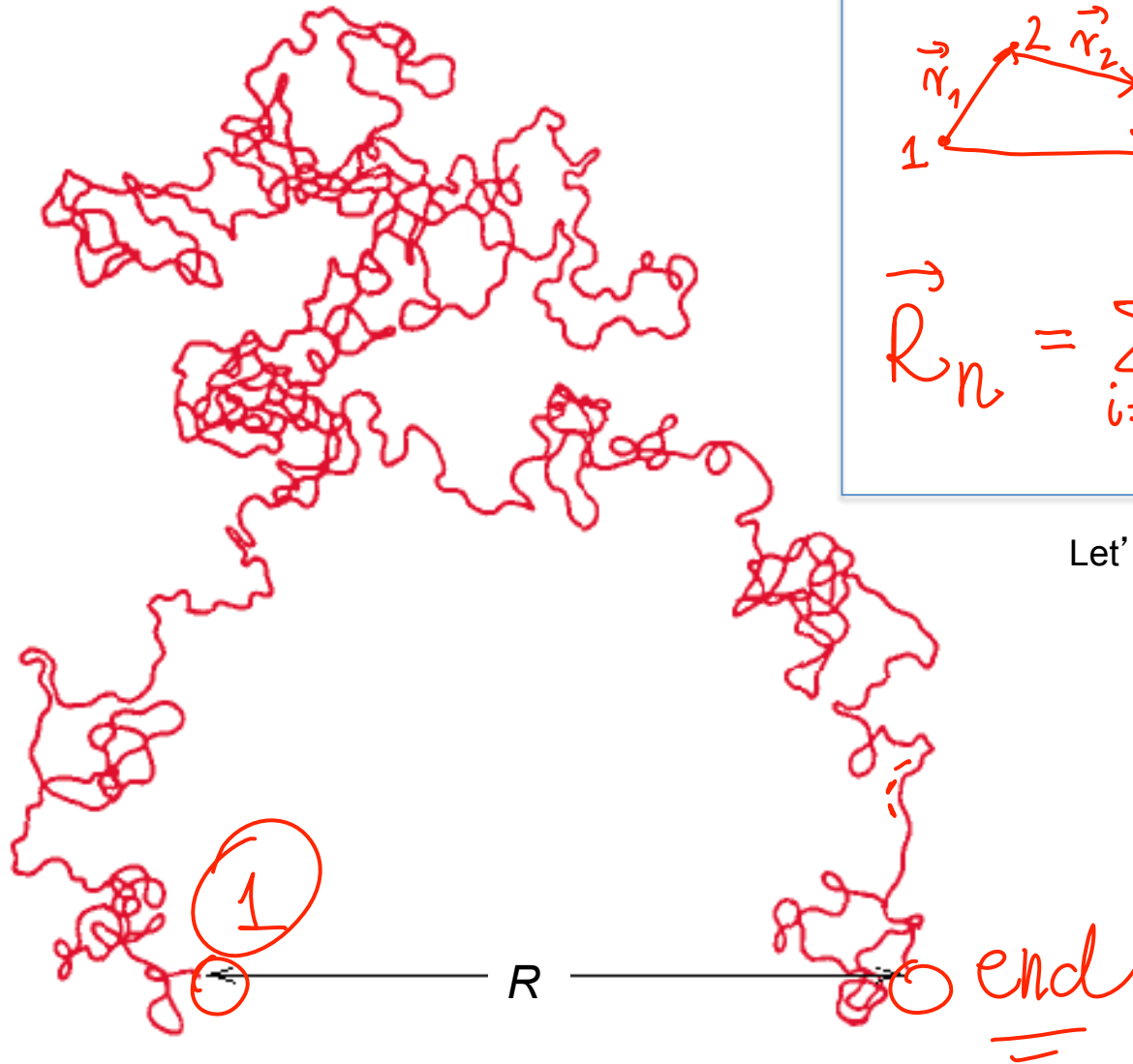
Lattice random walk



Variable angle random walk



Chain end-to-end distance



Let's define r , R , and l

however!

→
see next slide

Chain end-to-end distance

- Because of the equal probability of steps in each direction, the average end-to-end vector of a random walk of N steps, taken over many possible conformations (time average), is zero !!! not useful descriptor

$$\langle \vec{R}_n \rangle = 0 \quad \text{average over an ensemble } \langle \dots \rangle_n$$

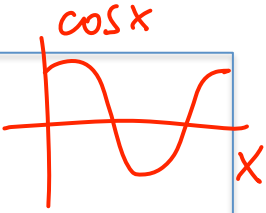
- The root-mean-square (rms) end-to-end distance, however, is finite, and characterizes the average spatial dimension traversed.


$$R_0 = \sqrt{\langle R_n^2 \rangle} = \sqrt{\langle \vec{R}_n \cdot \vec{R}_n \rangle} \neq 0$$

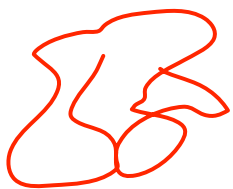


Chain end-to-end distance

$$\begin{aligned}
 R_0^2 = \langle R_n^2 \rangle &= \langle R_n \cdot R_n \rangle = \left\langle \sum_{i=1}^n \vec{r}_i \cdot \sum_{j=1}^n \vec{r}_j \right\rangle \\
 &= \underbrace{\sum_{i=1}^n r_i^2}_{n \cdot l^2} + \sum_{i \neq j}^n \vec{r}_i \cdot \vec{r}_j \\
 &= \underline{\underline{n \cdot l^2}} + 2 \cdot n \cdot l^2 \cdot \sum_{\substack{i \neq j \\ j \ll n}} \cos \theta_{ij}
 \end{aligned}$$







$$R_0 = \sqrt{\langle R_n^2 \rangle} = \sqrt{n \cdot l^2} = \underline{\underline{l \cdot n^{1/2}}}$$

scaling exponent

Some math...

Structure-property relationship of polymers

- **Consequence of this analysis:** polymer chain has a characteristic size that scales with $n^{1/2}$.
- **The average volume occupied by the coil is therefore much greater than the volume of the chain itself.**
- In the melt or glassy state, many other chains will be found intermingled with a single chain
- This is very different than in the case of small molecule systems, and leads to the unique rheological and mechanical properties polymers exhibit, like high viscosity and elasticity of polymers

$$V_{\text{coil}} \sim R_0^3 \sim n^{3/2}$$

$$V_{\text{chain}} = n \cdot V_{\text{monomer}} \sim n$$

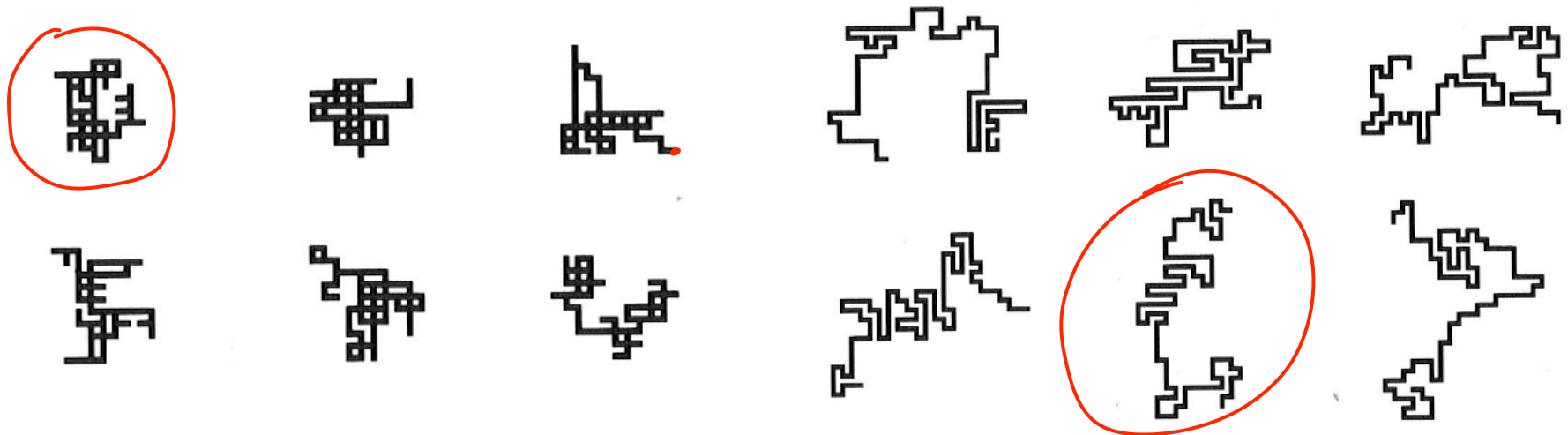
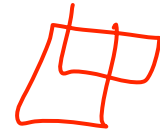
$$V_{\text{coil}} / V_{\text{chain}} \sim n^{1/2}$$

Volume of the chain and of the occupied volume

Self-avoiding random walk model

- We made certain assumptions so far - which ones?
- In solutions, polymers take on coil-like conformations, but are swelled due to monomer-solvent interactions
- The swelling can be explained by the random walk model: individual steps cannot cross each other

- $|\vec{r}_i| = \ell$
- independent steps
- angles arbitrary



$$\langle R^2 \rangle_{RWM}^{1/2} \propto N^{1/2}$$

$$\langle R^2 \rangle_{SARWM}^{1/2} \propto N^{3/5} \text{ swelling}$$

different scaling factor

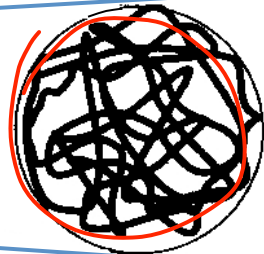
Polymer chain conformation

$$R_0 \propto N^\nu$$

scaling factor

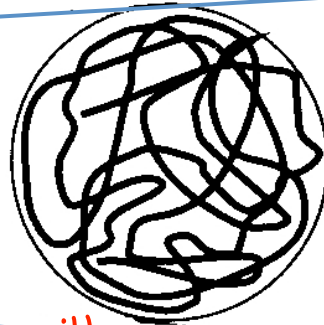
Collapsed coil

$$n = 1/3$$



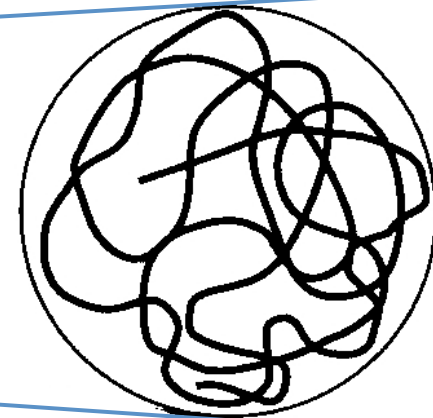
Random-walk coil

$$n = 1/2$$



Self-avoiding walk coil

$$n = 3/5$$



which of these will be relevant depends on a solvent, polymer side-chains etc. (details of the interaction between polymer chains and the solvent)

Assessment questions and keywords

1. How would you change the glass transition temperature of a non-crystalline material?

Keywords:

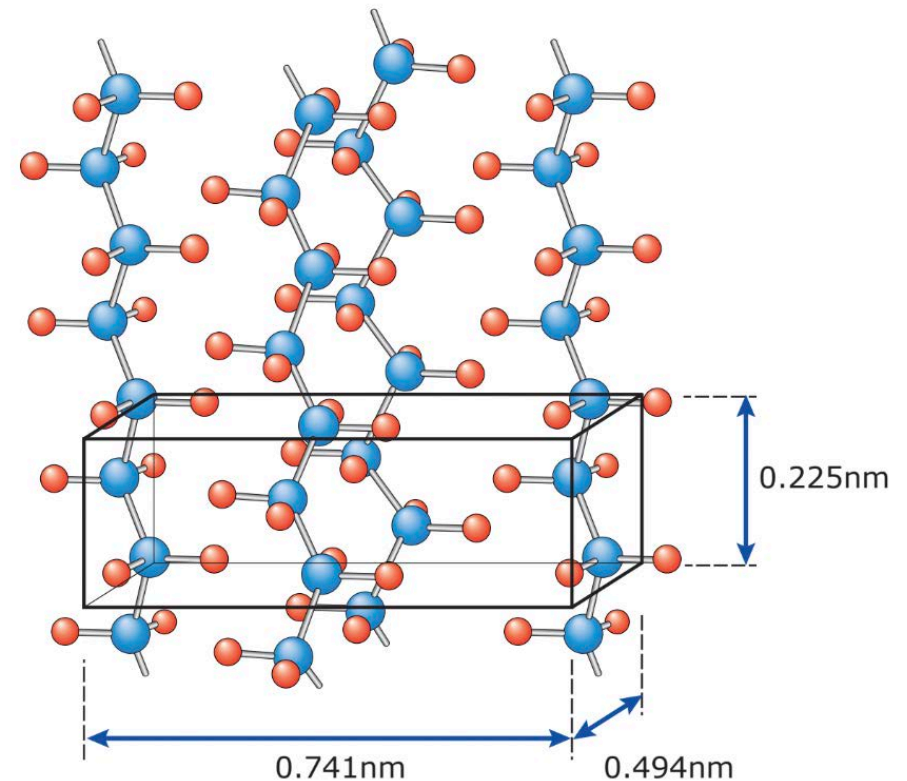
- network model
- network modifiers
- random walk model
- polymer conformation

Polymeric glasses and crystals

- Polymer glasses are rather common because of a large number of possible polymer conformations
- However, crystallization of polymers is possible: ordered atomic arrangements involving molecular chains

• **From what we know so far, what is a guaranteed way to ensure noncrystallinity of a polymer?**

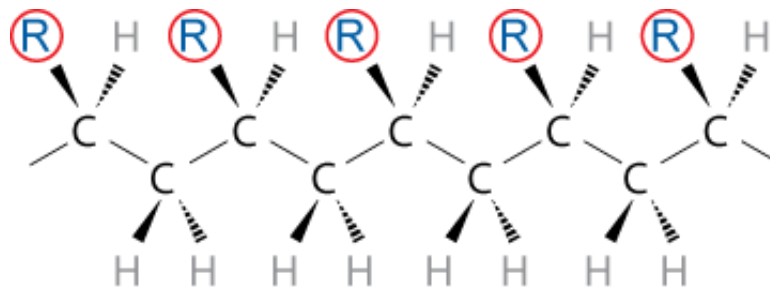
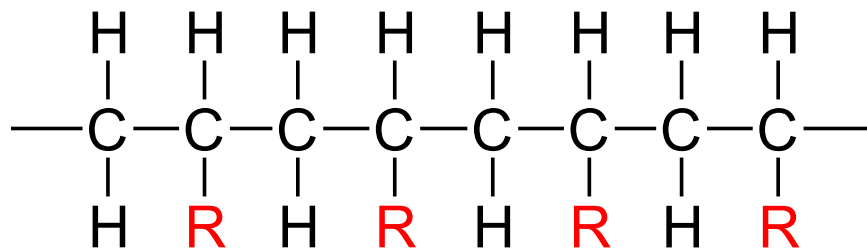
Polyethylene unit cell



Polymer tacticity

- For polymers having more than one side atom/group, the regularity and symmetry of the side group arrangement can significantly influence the properties
- **Tacticity** – stereoregularity or spatial arrangement of **R** units along chain

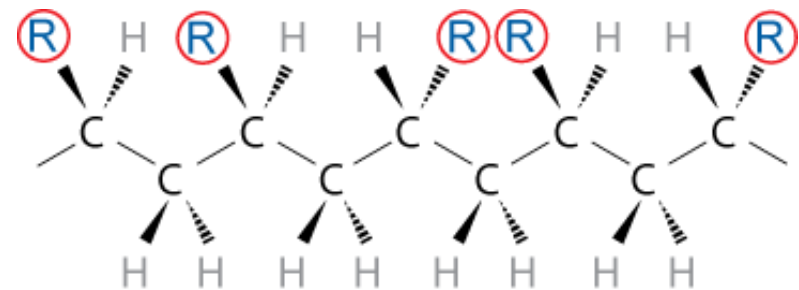
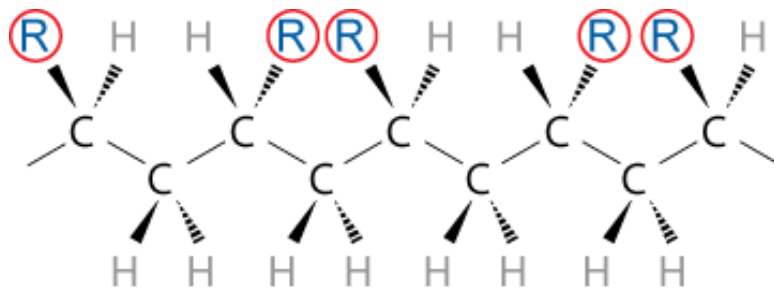
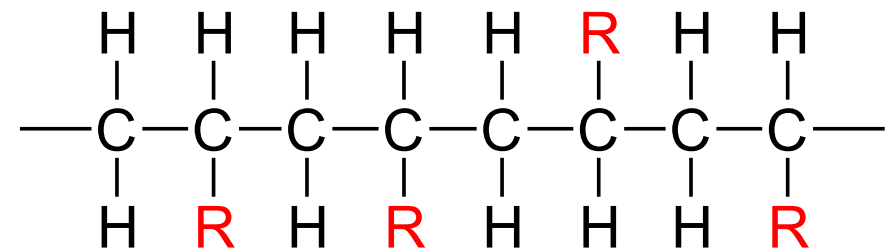
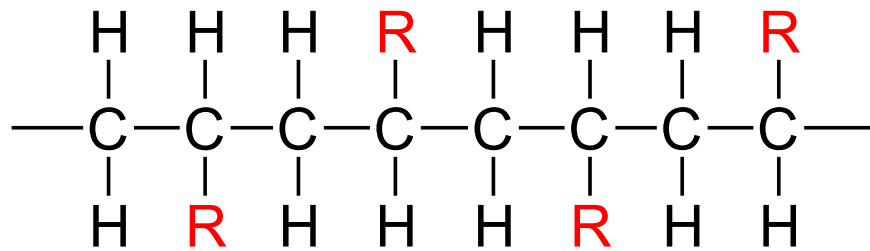
isotactic – all **R** groups on same side of chain



Polymer tacticity

syndiotactic – R groups
alternate sides

atactic – R groups randomly
positioned



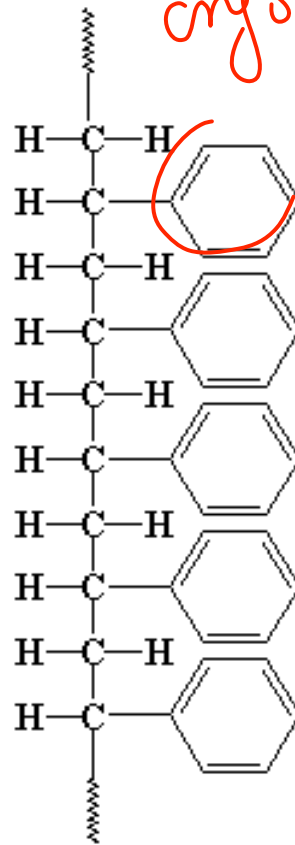
Polymer tacticity

One example (apparently a simple one) is polystyrene:

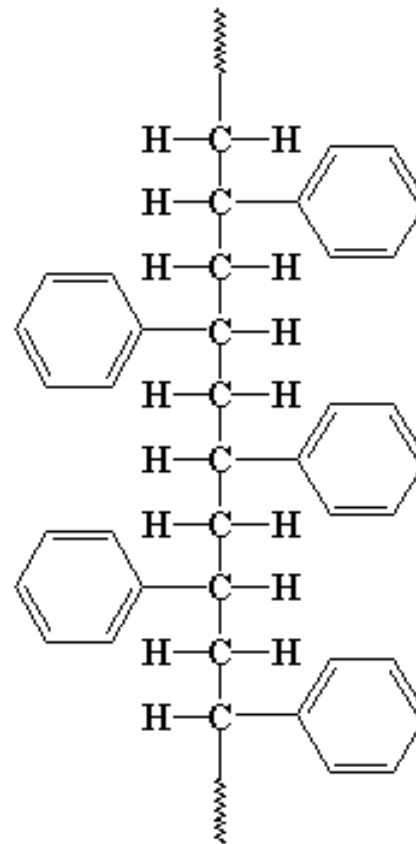
can crystallize

amorphous
↓

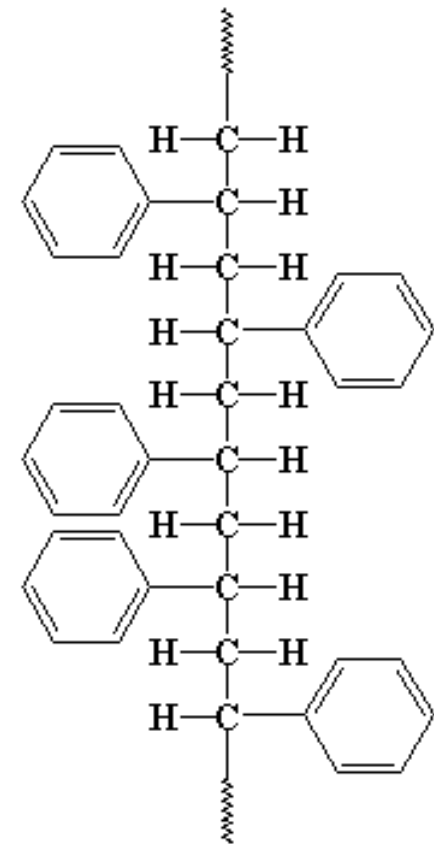
Styrene: C_8H_8



Isotactic



Syndiotactic



Atactic

Thermoplastics and thermosets

- What happens with properties of polymers with increased temperature?

1 Thermoplastics:

- soften when heated (and eventually liquefy) and harden when cooled
- process is reversible and may be repeated (materials can be recycled)
- bonds between individual molecules is relatively weak in thermoplastics (e.g. van der Waals bonding)
- above glass temperature, polymer molecules can slide and
- examples: polyethylene, polystyrene, poly(vinyl chloride)

Thermoplastics and thermosets

- What happens with properties of polymers with increased temperature?

2. Thermosets (thermosetting polymers)

- permanently hard (permanent curing), do not soften upon heating
- network polymers that are covalently linked
- at high temperature become damaged and degraded
- examples: vulcanized rubbers, epoxies, polyamides...

Fractals

- can be described as "a rough or fragmented geometric shape that can be split into parts, each of which is (at least approximately) a reduced-size copy of the whole"
- self similarity
- mass of a fractal does not scale with the dimension of the space

$$\underline{M} \propto \underline{R}^D$$

M : mass

R : characteristic length

D : scaling exponent, that is different than the space dimension (e.g. a fractal in 3 dimensional space will have $D \neq 3$)

Examples of fractals

- Diffusion limited aggregation
- Electrodeposition
- Metal crystallization – dendritic growth



Non-crystalline materials: summary

- short-range order
 - processing-dependent
(non-cryst. or cryst.)
 - many materials will form non-cryst. mater.
 - 2 very common: glasses & polymers
 - network model
 - random-walk model
- generic descriptors:
1. free V
2. PDF
-
- ```
graph TD; A["many materials will form non-cryst. mater."] --> B["generic descriptors:"]; B --> B1["1. free V"]; B --> B2["2. PDF"]; C["glasses & polymers"] --> D["network model"]; C --> E["random-walk model"];
```

# Structure of materials - roadmap

